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Phase equilibria in the Tl_2MoO_4–$R_2(MoO_4)_3$–$Zr(MoO_4)_2$ (R = Al, Cr) systems: synthesis, structure and properties of new triple molybdates $Tl_5RZr(MoO_4)_6$ and $TlRZr_{0.5}(MoO_4)_3$

The Tl_2MoO_4–$R_2(MoO_4)_3$–$Zr(MoO_4)_2$ (R = Al, Cr) systems were studied in the subsolidus region using X-ray powder diffraction and differential scanning calorimetric (DSC) analysis. Quasi-binary joins were revealed, and triangulation was carried out. New ternary molybdates $Tl_5RZr(MoO_4)_6$ (5:1:2) and $TlRZr_{0.5}(MoO_4)_3$ (1:1:1) (R = Al, Cr) were prepared. The unit cell parameters for the new compounds were calculated.

Keywords: phase equilibria, synthesis, systems, thallium, zirconium, iron, aluminum, crystal structure, space group.

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Introduction

This paper is a continuation of our systematic studies of phase relations in the Tl_2MoO_4–$R_2(MoO_4)_3$–$A(MoO_4)_2$ (R – trivalent metals, A = Zr, Hf) ternary salt systems [1]. Earlier we studied phase equilibria in the Tl_2MoO_4–$Fe_2(MoO_4)_3$–$Hf(MoO_4)_2$ system [2]. Subsolidus phase diagrams for this system and constituent double systems were constructed, and triple molybdates $Tl_5FeHf(MoO_4)_6$ and $TlFeHf_{0.5}(MoO_4)_3$ had been detected. The aims of the present study include (1) investigation of phase equilibria in the ternary salt systems Tl_2MoO_4–$R_2(MoO_4)_3$–$Zr(MoO_4)_2$ (R = Al, Cr), (2) determination of optimal condition for the solid state synthesis of ternary molybdates found in these systems, and (3) determination of crystallographic and thermal characteristics of the obtained compounds.

Experimental

Subsolidus phase relations in the Tl_2MoO_4–$R_2(MoO_4)_3$–$Zr(MoO_4)_2$ (R = Al, Cr) systems were studied in the subsolidus region (500–550 °C) using the intersecting joins method.

The corresponding molybdates of thallium, aluminum, chromium and zirconium were used as initial components for studying the phase equilibria in the Tl_2MoO_4–$R_2(MoO_4)_3$–$Zr(MoO_4)_2$ (R = Al,

Cr) systems. Synthesis of Tl_2MoO_4 was carried out according to the reaction $Tl_2O_3+MoO_3 \rightarrow Tl_2MoO_4+O_2\uparrow$ at gradually increasing temperature in the range 400–550 °C for 50 h. The high temperature modification of $Zr(MoO_4)_2$ was prepared by annealing of stoichiometric mixture of binary oxides ZrO_2 and MoO_3 at 400–700 °C for 100 h. Aluminum molybdate and chromium molybdate were obtained by calcination of stoichiometric mixtures of precursors $Al(NO_3)_3 \cdot 9H_2O$, Cr_2O_3, and MoO_3 in the temperature range 400–650 °C for 100 h. The initial stage of each synthesis was chosen as 400 °C since MoO_3 possesses high volatility at temperature about 600 °C. To ensure better homogenization, the reaction mixtures were ground in ethanol every 20–30 h during firing. After annealing, the samples were slowly cooled in the furnace. The non-equilibrium samples were additionally annealed. It was assumed that equilibrium is reached if the phase composition of the samples remains unchanged during two consecutive anneals. The crystallographic parameters of the synthesized compounds were close to those reported in literature [3–5].

X-ray powder diffraction (XRD) measurements were performed using Bruker D8 Advance diffractometer (Bragg–Brentano geometry, Cu Kα radiation, secondary monochromator, maximum angle $2\theta=100°$, scan step 0.02°). The differential scanning calorimetric (DSC) analysis of the samples was carried out using NETZCH STA 449C (Jupiter, Germany) thermoanalyzer. Compounds' pellets were placed in a Pt-crucible, heated up and then cooled down in argon atmosphere with the heating and cooling rate of 10 K/min.

Results and discussion

The information about the phase formation in the Tl_2MoO_4–$R_2(MoO_4)_3$–$Zr(MoO_4)_2$ (R = Al, Cr) systems, which represent the bounding sides of the studied system, were taken from previous papers [3–5]. The formation of double molybdates with general composition $TlR(MoO_4)_2$ was detected in the boundary Tl_2MoO_4–$R_2(MoO_4)_3$ systems [3]. Two double molybdates $Tl_8Zr(MoO_4)_6$ and $Tl_2Zr(MoO_4)_3$ were formed in the Tl_2MoO_4–$Zr(MoO_4)_2$ system [4]. No intermediate compounds were found in the $R_2(MoO_4)_3$–$Zr(MoO_4)_2$ systems [5].

In order to find new triple molybdates, the subsolidus phase equilibria in the Tl_2MoO_4–$R_2(MoO_4)_3$–$Zr(MoO_4)_2$ (R = Al, Cr) systems were studied at 500–550 °C and its triangulated phase diagrams were constructed. Solid-state interactions between Tl_2MoO_4, $R_2(MoO_4)_3$, and $Zr(MoO_4)_2$, which occurred over wide ranges of temperature and concentration, led to the formation of new triple molybdates $Tl_5RZr(MoO_4)_6$ (5:1:2 mole ratio) S_1 and $TlRZr_{0.5}(MoO_4)_3$ (1:1:1 mole ratio) S_2. Compound S_2 was found at the intersection point of the $R_2(MoO_4)_3$–$Tl_2Zr(MoO_4)_3$ and $TlR(MoO_4)_2$–$Zr(MoO_4)_2$ joins. The triple molybdate (S_1) locates inside the triangle with the double molybdates $TlR(MoO_4)_2$, $Tl_8Zr(MoO_4)_6$ and $Tl_2Zr(MoO_4)_3$ in its vertices.

The phase relations in the Tl_2MoO_4–$R_2(MoO_4)_3$–$Zr(MoO_4)_2$ (R = Al, Cr) systems are shown in Fig. 1.

Individual $Tl_5RZr(MoO_4)_6$ (R = Al, Cr) oxides were prepared by firing at 450–550 °C for 150–200 h, and the molybdates $TlRZr_{0.5}(MoO_4)_3$ (R = Al, Cr) were obtained by firing at temperatures from 500 to 600 °C for 100–150 h.

The single phase $Tl_5AlZr(MoO_4)_6$ was not synthesized under the conditions of our experiment.

The analysis of X-ray diffraction patterns of the compounds obtained shows that the reflection positions and their intensity ratio for $TlRZr_{0.5}(MoO_4)_3$ and $Tl_5RZr(MoO_4)_6$ (R = Al, Cr) are similar to $TlFeHf_{0.5}(MoO_4)_3$ [2] and $Rb_5ErHf(MoO_4)_6$ [6], respectively. It could be concluded that $TlRZr_{0.5}(MoO_4)_3$ is isostructural to $TlFeHf_{0.5}(MoO_4)_3$ and $Tl_5RZr(MoO_4)_6$ is isostructural to $Rb_5ErHf(MoO_4)_6$.

Three dimensional framework of the $TlFeHf_{0.5}(MoO_4)_3$ crystal structure (a = b = 13.0324(2) Å, c = 11.8083(3) Å, V = 1736.87(6) Å^3, ρ_{calc}=4.757 g/cm^3, space group $R\bar{3}$, Z = 6) is composed of the Mo-tetrahedra sharing O vertices with the (Fe, Hf)O_6 octahedra, with thallium atoms occupying wide channels in the framework [2] (Figs. 2 and 3). The arrangement of Tl atoms (pink spheres) in the structural channel in $TlFeHf_{0.5}(MoO_4)_3$ is shown in Fig. 3.

$Rb_5ErHf(MoO_4)_6$ possesses the trigonal crystal structure: a = 10.7511(1) Å, c = 38.6543(7) Å, V = 3869.31(9) Å^3, ρ_{calc}=4.462 g/cm^3, Z = 6, space group $R\bar{3}c$ [6]. The three-dimensional framework of the structure is formed of the MoO_4 tetrahedra, which are sharing corners with two ErO_6 and HfO_6 octahedra (Fig. 4). Two types of Rb atoms occupy large cavities in the framework. The particular ar-

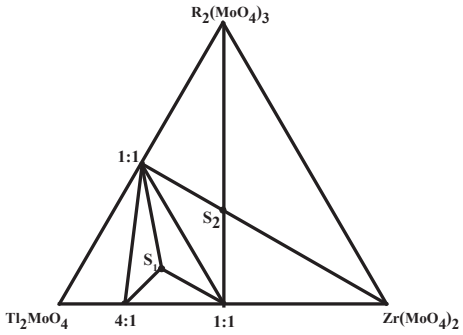

Fig. 1. Subsolidus phase relations in the Tl_2MoO_4–$R_2(MoO_4)_3$–$Zr(MoO_4)_2$ (R = Al, Cr) systems: S_1 –$Tl_5RZr(MoO_4)_6$ (5:1:2 mole ratio) and S_2 – $TlRZr_{0.5}(MoO_4)_3$ (1:1:1 mole ratio)

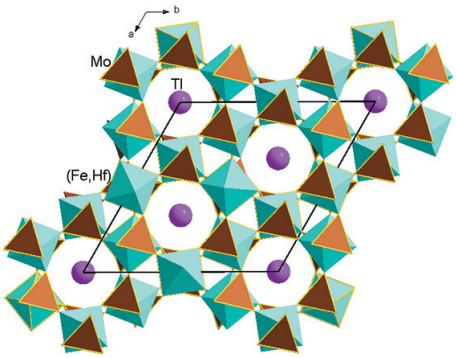

Fig. 2. The framework of $TlFeHf_{0.5}(MoO_4)_3$ crystal structure that consists of MoO_4 tetrahedra and (Fe, Hf)O_6 octahedra in the projection of layer onto the (001) plane (Tl atoms are represented by pink spheres)

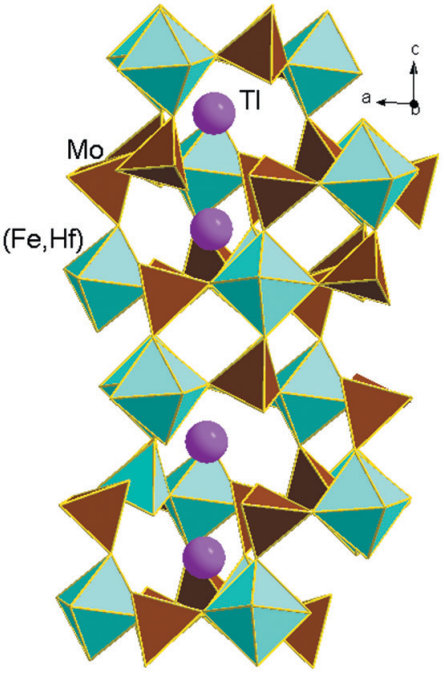

Fig. 3. The fragment of the $TlFeHf_{0.5}(MoO_4)_3$ crystal structure that is projected onto the (010) plane

rangement of Rb atoms in the structural channel is shown in Fig. 5. The distribution of the Er^{3+} and Hf^{4+} cations over two positions is obtained during the structure refinement.

The unit cell parameters for the synthesized triple molybdates $TlRZr_{0.5}(MoO_4)_3$ (R = Al, Cr) were refined using uniquely-indexed lines for the $TlFeHf_{0.5}(MoO_4)_3$ single crystal [2]. The lines for $Tl_5CrZr(MoO_4)_6$ were indexed using $Rb_5ErHf(MoO_4)_6$ [6] as analogous isostructural compound. The unit cell parameters that were refined using the TOPAS-4 software are listed in Table 1 along with the melting points of the corresponding compounds. Fig. 6 illustrates good coincidence of the experimental and calculated profiles.

As shown in Table 1, the unit cell parameters and volume of $TlRZr_{0.5}(MoO_4)_3$ (R = Al, Cr) and $Tl_5CrZr(MoO_4)_6$ increase with the substitution of 6-coordinated aluminum cations (r = 0.535 Å) with a larger chromium cation (r = 0.615 Å) [7]. The linear dependence of the unit cell volume on the trivalent element radii is also in accordance with $TlRZr_{0.5}(MoO_4)_3$ (R = Al,

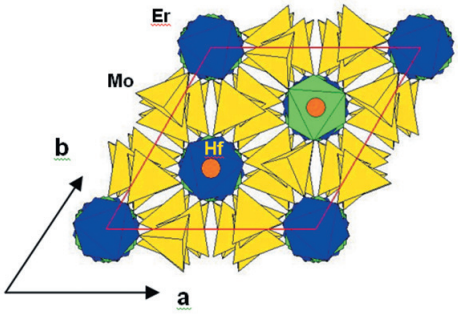

Fig. 4. Complex framework of the $Rb_5ErHf(MoO_4)_6$ crystal structure built of the MoO_4 tetrahedra and $(Er, Hf)O_6$ octahedra. Red parallelogram shows the projection of a layer onto the (001) plane. The Rb atoms are represented by the orange spheres

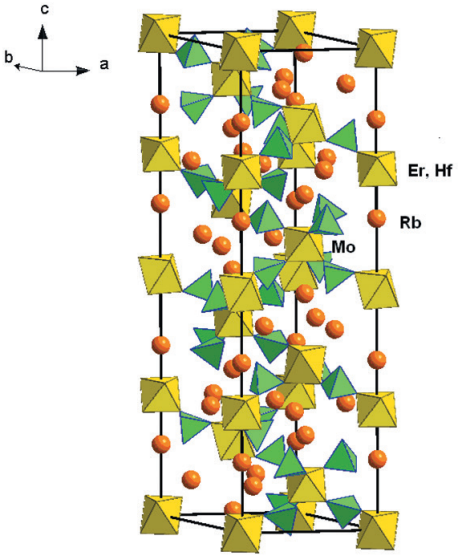

Fig. 5. Crystal structure of $Rb_5ErHf(MoO_4)_6$ as projected on plane (133)

Table 1

The unit cell parameters and melting points of $TlRZr_{0.5}(MoO_4)_3$ (R = Al, Cr) and $Tl_5CrZr(MoO_4)_6$ in comparison with literature data

Compound	Unit cell parameters (Å)				T, °C
	a, Å	c, Å	V, Å^3	space group; Z	
$TlFeHf_{0.5}(MoO_4)_3$ [2]	13.0324(2)	11.8083(3)	1736.87(6)	$R\bar{3}$; 6	811
$TlAlZr_{0.5}(MoO_4)_3$	12.5935(6)	11.5946(8)	1592.5(2)		751
$TlCrZr_{0.5}(MoO_4)_3$	12.6961(6)	11.7022(9)	1633.6(2)		842
$Rb_5ErHf(MoO_4)_6$ [6]	10.7511(1)	38.6543(7)	3869.31(9)	$R\bar{3}c$; 6	730
$Tl_5CrZr(MoO_4)_6$	10.4047(8)	37.5322(3)	3518.8(6)		599

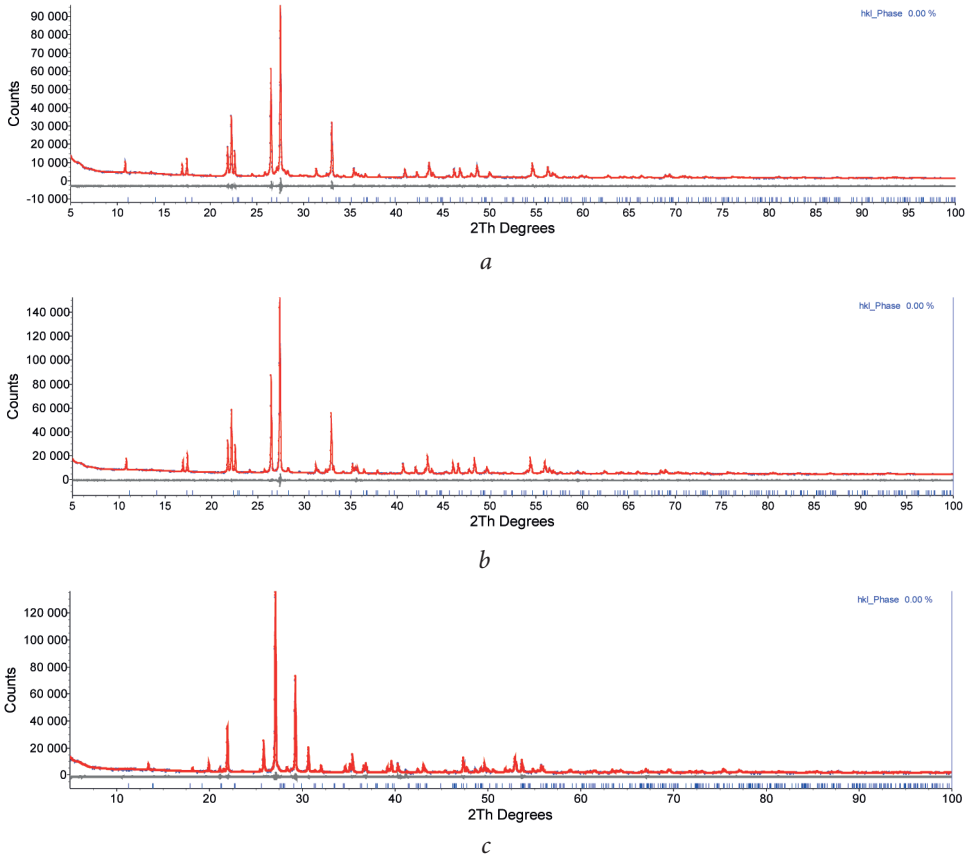

Fig. 6. Measured (red), calculated (black) and differential (blue) powder diffraction patterns for $TlCrZr_{0.5}(MoO_4)_3$ (*a*), $TlAlZr_{0.5}(MoO_4)_3$ (*b*) and $Tl_5CrZr(MoO_4)_6$ (*c*)

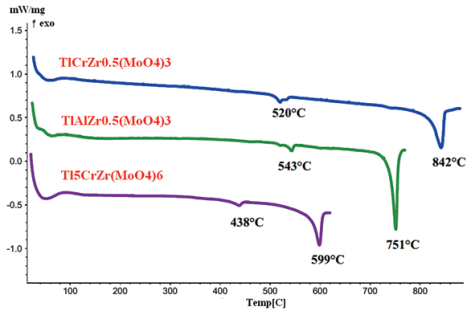

Fig. 7. DSC curves for $TlRZr_{0.5}(MoO_4)_3$ (R = Al, Cr) and $Tl_5CrZr(MoO_4)_6$

Conclusions

New triple molybdates with general compositions $Tl_5RZr(MoO_4)_6$ (5:1:2) and $TlRZr_{0.5}(MoO_4)_3$ (1:1:1) (R = Al, Cr), respectively, were obtained in the thallium-containing systems with trivalent metals and zirconium. The formation of these triple molibdates occurs similarly to the formation of ternary molibdate $Tl(FeHf_{0.5})$ Cr) and $Tl_5CrZr(MoO_4)_6$ belonging to one structural family.

Two endothermic effects are observed on the DSC curves (Fig. 7). The first one corresponds to some structural changes that, however, are not accompanied by the change of a structural type. The last endothermic effect corresponds to the melting of the studied compounds.

$(MoO_4)_3$ in previously studied Tl_2MoO_4–$Fe_2(MoO_4)_3$–$Hf(MoO_4)_2$ system [2]. The phase relations do not change with hafnium (r = 0.71 Å) being substituted with zirconium (r = 0.72 Å) [7].

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References

1. Grossman VG, Bazarov BG, Bazarova ZhG. Subsolidus phase diagrams for the Tl_2MoO_4–$Ln_2(MoO_4)_3$–$Hf(MoO_4)_2$ systems, where Ln = La–Lu. *Russ J Inorg Chem.* 2008;53(11):1788–94. DOI:10.1134/S003602360811020X
2. Grossman VG, Bazarov BG, Klevtsova RF, Glinskaya LA, Bazarova ZhG. Phase equilibria in the Tl_2MoO_4–$Fe_2(MoO_4)_3$–$Hf(MoO_4)_2$ system and the crystal structure of ternary molybdate $Tl(FeHf_{0.5})(MoO_4)_3$. *Russ Chem Bull.* 2012;61(8):1546–9. DOI:10.1007/s11172-012-0202-7
3. Pleskov MY, Morozov VA, Lazoryak BI, Zhizhin MG, Burdakova IB, Khalbaeva KM, Tsyrenova GD, Khaikina EG. Structures of double molybdates $TlR(MoO_4)_2$ (R = In, Sc, Fe, Cr, Al). *Russ J Inorg Chem.* 2005(4);50:604–14.
4. Bazarov BG, Klevtsova RF, Bazarova TsT, Glinskaya LA, Fedorov KN, Bazarova ZhG, Chimitova OD. Systems Tl_2MoO_4–$E(MoO_4)_2$, where E = Zr or Hf, and the crystal structure of $Tl_8Hf(MoO_4)_6$. *Russ J Inorg Chem.* 2006;51(5):794–9. DOI:10.1134/S0036023606050184
5. Tushinova YuL, Bazarova ZhG, Archincheyeva SI. Abstracts of the reports. Ulan-Ude (Russia): Publishing house of BSC SB RAS; 2002. p. 90–1. Russian.
6. Bazarov BG, Klevtsova RF, Chimitova OD, Glinskaya LA, Fedorov KN, Tushinova YuL, Bazarova ZhG. Phase formation in the Rb_2MoO_4–$Er_2(MoO_4)_3$–$Hf(MoO_4)_2$ system and the crystal structure of new triple molybdate $Rb_5ErHf(MoO_4)_6$. *Russ J Inorg Chem.* 2006;51(5):800–4. DOI:10.1134/S0036023606050196
7. Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst.* 1976;A32:751–67. DOI:10.1107/S0567739476001551

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